Sources and controls of calcium and magnesium in storm runoff: the role of groundwater and ion exchange reactions along water flowpaths

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Sources and controls of calcium and magnesium in storm runoff: the role of groundwater and ion exchange reactions along water flowpaths

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Abstract

A combined hydrological and chemical investigation was undertaken in a small moorland catchment at Plynlimon to determine the processes controlling storm runoff chemistry. Flow from natural soil pipes, overland flow from peat soils, throughflow from a mineral horizon and streamflow were gauged and sampled intensively during seven storms. Stormflow Ca and Mg concentrations in stream water consistently exceeded those observed in overland flow, pipeflow and throughflow. The response of Ca and Mg to increases in streamflow varied between the storms and could not be explained readily by the mixing of the dominant source waters monitored within the catchment. Intensive sampling of pipe water along a major stormflow pathway revealed a large and consistent increase in the concentration of dissolved Ca and Mg accompanied by a corresponding decrease in acidity, the magnitude of which was strongly influenced by antecedent conditions. Analyses of soil exchangeable cations along the stormflow pathway revealed soils enriched in divalent cations probably derived from a groundwater source. Laboratory leaching experiments confirmed that rapid cation exchange reactions could explain the changes in pipe water chemistry along the stormflow pathway. The relative contribution of flow from pathways where these ion exchange reactions occur strongly influences the stormflow response of Ca and Mg in the stream. The results also highlight a potentially important, indirect role for base-rich groundwater in modifying storm runoff chemistry along water flowpaths.

Introduction

For more than a decade, considerable research effort has been directed towards the conceptualisation and modelling of the episodic hydrochemical variations observed in upland streams in response to stormflow events (Reid *et al.*, 1981; Muscutt *et al.*, 1990; Jenkins *et al.*, 1994). During these events, the predominant water pathways are thought to change from deeper sources, rich in base cations derived from weathering, to shallower organic horizons with acidic waters (Vogt *et al.*, 1990; Chapman *et al.*, 1993; Muscutt *et al.*, 1993). However, due to the difficulties of studying these systems, knowledge of the complex hydrological processes that operate during storms is often incomplete (Bishop *et al.*, 1990). As a result, several different approaches have been used to determine the hydrological and hydrochemical response of catchment waters to storms.

Recognition of ambiguity in process identification using conceptual hydrochemical models has led to the application of simple hydrograph analysis techniques (Beck *et al.*, 1990; Wheater and Beck, 1995). Hydrograph separation techniques using steady state mass balance equations for water and chemical tracers, such as chloride and stable isotopes of oxygen and hydrogen have been used to determine the contribution of old (pre-event) and new (event) water to the storm hydrograph (Sklash *et al.*, 1986; Pearce *et al.*, 1986; Ogunkoya and Jenkins, 1991). A recent development from this has been end member mixing analysis (EMMA) which attempts to determine the proportion of different source waters to streams during storms by linking soil and baseflow water chemistries with observed stream water chemistry under the assumption that stream water comprises a mix of source waters with distinct and characteristic chemical compositions (e.g. Christophersen *et al.*, 1990; Hooper *et al.*, 1990; Robson and Neal, 1990). In parallel field studies, various approaches have been made to undertake frequent, simultaneous hydrological and hydrochemical observations (e.g. Bishop *et al.*, 1990; Muscutt *et al.*, 1990; Chapman, 1994) to provide a high temporal resolution data base from which to develop conceptual and process models (e.g. Hutchins *et al.* 1996).

The Plynlimon catchments have provided a particular focus for both the development of intensive field studies and the application of EMMA techniques. However, both approaches have encountered difficulties in explaining the stormflow hydrochemical response in terms of observed source water chemistries. Many applications of EMMA suggest that base-rich 'groundwater' or water with a long residence time within the catchment provides a major input to streamflow during storms, often exceeding that from the soil horizons (Christophersen *et al.*, 1990; Robson and Neal, 1990; Neal *et al.*, 1990). The rapid delivery of large volumes of groundwater to the stream during storms is not easily explained. Sklash and Favolden (1979) proposed groundwater ridging as the dominant process. However, this process is limited to the near stream area. Alternatively, rapid water movement through permeable drift deposits may occur (Knapp, 1970; Jenkins *et al.*, 1994). However, a large contribution of groundwater to streamflow during storms does not appear to be consistent with i) hydrochemical observations such as the increase in stream water DOC content and acidity during storms (e.g. Muscutt *et al.*, 1990; Bishop *et al.*, 1990), which is attributed to changes in water flowpaths from deep to upper horizons of the soil or ii) results from hydrological studies which show that flow along preferential pathways within the upper soil horizons is the dominant mechanism for the transport of runoff during storms in upland catchments (Chappell *et al.*, 1990; Mulder *et al.*, 1990; Wheater *et al.*, 1991; Soulsby, 1992). Notwithstanding some useful and detailed results, field studies using an integrated approach of hydrological monitoring and chemical sampling, have also failed to yield a complete understanding of the system other than perhaps highlighting the potential for groundwater sources. In the C2 catchment at Plynlimon, Muscutt *et al.* (1990; 1993) found that stream water chemistry often did not reflect the chemistry of the inferred source waters. These observations were attributed to chemical processes occurring along stormflow pathways (Muscutt *et al.*, 1990; 1993), although without direct evidence. With such discrepancies also reported elsewhere (Christophersen *et al.*, 1990; Neal *et al.*, 1990) a major gap in the understanding of mechanisms controlling storm runoff chemistry was apparent.

An integrated approach of hydrological and chemical monitoring and intensive sampling of catchment waters during storms was initiated in the C2 catchment at Plynlimon to determine the spatial and temporal variability of hydrological and chemical processes within the catchment and their influence in controlling the chemical response of stream water during storms. This paper describes the role of groundwater in modifying the chemistry of soils along preferential water flowpaths and its effect on the Ca and Mg concentration of storm runoff.

Site Description

The C2 catchment is a first order tributary of the headwaters of the River Wye draining the eastern slopes of Plynlimon, mid-Wales (Fig. 1). The catchment has an altitude range of 400–510 m above sea-level, an area of approximately 4 ha and a ten year (1980–1990) mean annual rainfall of 2605 mm. The Plynlimon massif is composed of Ordovician slates and Silurian mudstones of the Lower Palaeozoic era, with the imprint of Quaternary glaciation and periglaciation. Major faulting occurs within the Wye catchment in a north-south to northeast-southwest direction, the main faults being the East and West Cyff Faults, of which the East Cyff Fault passes close to the C2 catchment (Chapman, 1986). The C2 catchment is underlain by mudstone from the Frongoch series (Middle Llandovery series (Silurian)). The major soils are acid, nutrient-poor stagnopodzols and peats which have developed on solid shale or derived colluvium and soliflucted material, the thickness of which can vary from a few cm to 2 m (Knapp, 1970). The stagnopodzols, covering 55% of the catchment, occur predominantly on the gentler (10–15°), more freely draining, upper slopes of the catchment. Peat, which covers 30% of the catchment, occurs in two distinct regions; at the hilltop and around the stream head. Small areas of brown earth, peaty gley and ranker soils occur in the steep sided stream hollow. Vegetation consists of an acid grassland dominated by *Nardus* and *Festuca* species with *Eriophorum sp.* on the peats. The catchment has no history of agricultural improvement by liming or fertiliser addition and supports low density sheep grazing for most of the year.

An extensive network of natural soil pipes is found at the base of the organic horizon within the stagnopodzols, exhibiting a morphology similar to that described by Gilman and Newson (1980). Pipe flow is ephemeral but occurs throughout the year in response to rainfall events, with discharges of up to 9.8 l s^{-1} recorded at the largest pipe outlet (PA in Fig. 1), although flows of less than 4 l s^{-1} are more common (Chapman, 1994). During events, the mean contribution of peak pipeflow from outlet PA to maximum stream discharge is about 10% with a range from 3.3% during long duration, low intensity rainfall to a maximum of 32% associated with short, high intensity storms (Chapman, 1994). Similar behaviour has been observed by Jones (1990) in the nearby Maesnant catchment.

The pipe network allows a large area of the catchment to contribute to storm runoff (Muscutt *et al.*, 1993) and is an important pathway for runoff generated on the hilltop peat as well as from within the podzols. However, the catchment-wide contribution of pipeflow to total storm runoff is difficult to determine as pipeflow data have only been collected at the largest outlet (Chapman, 1994). In addition, no pipes emit directly into the stream due to the change in slope and soil type close to the stream channel;

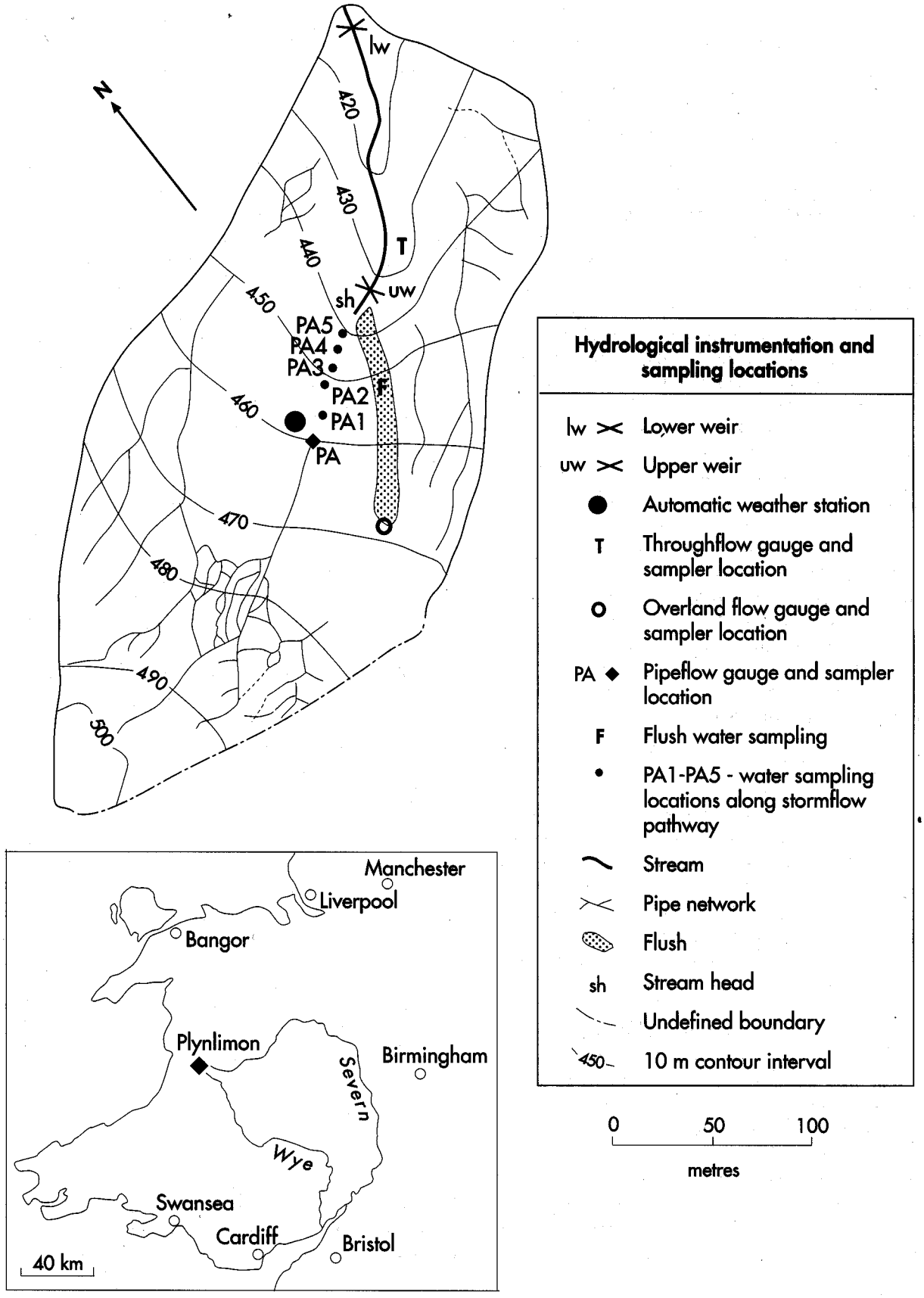

Fig. 1. *Map of the C2 catchment showing hydrological instrumentation and sampling locations.*

typically, they discharge over peat soils as overland flow. The water emitted at pipe outlet PA takes a well defined pathway from the outlet, flowing rapidly over the surface of the peat soil for 30 m, which is usually saturated, to a hollow at the head of the stream. The water then flows either overland or via a series of small channels within peaty ranker soils and weathered bedrock material for 25 m to reach the stream. It is therefore likely that much of the water emitting here contributes to stormflow.

The peat around the stream head is saturated for much of the year and generates overland flow. Extrapolation of hydrometric overland flow responses measured from peat soils at the head of the flush (based on the area estimated to be contributing to the gauge and the area of peat soils) suggests that overland flow contributes approximately 50% of peak streamflow recorded at the catchment outlet (Muscutt *et al.*, 1993; Chapman, 1994). Much of this overland flow is intercepted by the flush (Fig. 1), a narrow strip of permanently saturated mire, which allows a large volume of overland flow to reach the stream channel rapidly during storms. Throughflow from a mineral soil horizon at an exposed soil face in a topographic hollow on the eastern sideslope also contributes to storm runoff, although the response is strongly dependent on antecedent conditions (Chapman, 1994). The groundwater component of stormflow in this catchment is believed to be small, due to the low vertical permeability of the soils, indicated by the high flow rates from surface soils (Muscutt *et al.*, 1993).

Materials and Methods

CATCHMENT INSTRUMENTATION AND STORM SAMPLING

Rainfall was recorded by a 0.18 mm tipping bucket gauge at five minute intervals at an automatic weather station located centrally within the catchment. To characterise and quantify the response of; (1) pipeflow at outlet PA, (2) overland flow at the head of the flush (O) and (3) throughflow from a mineral horizon on the sideslope of the stream (T) (Fig. 1), tipping bucket gauges were installed and counted electronically by pulses from a reed switch. Stream discharge was recorded at two locations; 40 m below the stream source and at the catchment outlet, using a 90° V-notch weirs and water level recorders connected to solid state data loggers (Fig. 1). The discharge at the weirs was calculated using the standard equation for a 90° thin plate weir (British Standards Institution, 1981). Calibration of the stream flow was carried out at low flows using a 18 litre bucket and stopwatch. The results obtained suggests that the use of the standard equation introduces less than 10% error at low flows at the catchment outlet (Muscutt, 1991) and 11% at low flows at the upper weir (Chapman, 1994).

During the study period from June 1991 to December 1992, seven storms were sampled intensively; 10 June 1991, 3 July 1991, 24 July 1991, 31 October 1991, 1 November 1991, 10 March 1992 and 11 March 1992. Stream water was collected every 0.25–2 h at the catchment outlet using an automatic sampler. Grab samples of the major source waters; (1) pipe at outlet PA, (2) overland flow at location O, (3) flush water at location F and (4) mineral soil throughflow at location T, were collected in polypropylene bottles at approximately regular intervals (between 1 and 2.5 h) throughout each event. Water samples from the soil surface were also collected at regular intervals (between 1 and 2.5 h) from five points (PA1-PA5) along the stormflow pathway between pipe outlet PA and the stream channel to determine whether the chemical composition of pipe water remained constant between its source and the stream channel. The locations of all sampling points are indicated in Fig. 1.

SOIL SAMPLING AND ANALYSIS

Soil was sampled at depths of 0–10 cm, 10–30 cm and >30 cm, where possible as the soil was very shallow. At seven locations along the stormflow pathway between pipe outlet PA and the stream channel. Exchangeable cations were determined on duplicate samples by extraction of 5 g of fresh field-moist soil with 100 ml of 0.1 M $BaCl_2$ solution (Hendershot and Duquette, 1986). The solution was filtered through Whatman No. 542 filters, pre-washed with a small amount of $BaCl_2$ and analysed for Na and K by flame emission and Ca, Mg and Al by flame atomic absorption spectrophotometry. A pressure calcimeter was used to measure 'free lime' ($CaCO_3$) on samples of air-dried soil (Avery and Bascombe, 1974).

LABORATORY INVESTIGATION OF ION EXCHANGE REACTIONS

In a laboratory simulation experiment to reproduce the changes in pipe water chemistry observed in the field, eighty grammes of field-moist soil from the 0–10 cm depth at location 2 was placed in a small piece of guttering (20 cm long by 3 cm wide) and ten 100 ml samples of pipe water were released from a separating funnel at a rate of approximately 1 ml s^{-1} and passed sequentially over the soil. The pipe water flowed mainly over the surface of the soil (i.e. as overland flow) before passing into a funnel and Whatman No. 41 filter paper placed in the neck of a conical flask.

CHEMICAL ANALYSIS OF WATER SAMPLES

All water samples were analysed for pH prior to filtration through 0.45 μm pore size membranes. Calcium and Mg were analysed by flame atomic absorption spectrophotometry.

Storm Hydrology

The monthly rainfall characteristics recorded at the C2 automatic weather station and at the ITE monthly rainfall collector, situated just outside the catchment, for the period June 1991 to December 1992 are shown in Table 1. Although the 1992 annual rainfall of 2557 mm is close to the ten year (1980–1990) average of 2605 mm, several extended periods with low or no rainfall occurred during the study. In June 1992, only 38% of the ten year (1980–1990) mean rainfall for that month was recorded and other months, such as October 1991, January, February and December 1992 were also noticeably drier than the ten year average monthly rainfall. In contrast, the three month period June to August 1991 was 14% wetter than average and other wet months were March 1992, August 1992 and November in both 1991 and 1992.

Precipitation occurred in the catchment on approximately three in every four days, although almost half the wet days received less than 5 mm. Rainfall events (defined as rainfall that produces a runoff response in the stream of > 10 l s^{-1}) occurred throughout the year (Table 1) and varied in size from <10 mm to 136 mm. However, the majority of rainfall events (58%) ranged between 20 and 40 mm and only 15% of rainfall events exceeded 40 mm.

The stream hydrograph is dominated by the dynamic response to individual storm events. The stream is perennial, but flow during the summer can be very low and baseflow was generally less than 2 l s^{-1}. During the period June 1991 to December 1992, inclusive, stream discharge at the catchment outlet ranged between 0.17 l s^{-1} (3 June 1991) and 88.1 l s^{-1} (28 March 1992) and total runoff for the period, minus 38 days, was 3341 mm, of which 77% occurred as stormflow (> 2 l s^{-1}). If it is assumed that all flow below 2 l s^{-1} is baseflow, the ratio of total baseflow (< 2 l s^{-1}) to the total runoff gives a value of 0.23, which is a measure of the flow derived from groundwater or slow throughflow processes. During the study period there were 84 peaks in excess of 10 l s^{-1}, with the majority of peaks, 51, ranging between 10 and 30 l s^{-1}; in only 14 storms did peak flow exceeded 30 l s^{-1}.

An antecedent runoff index (ARI) has been derived for the catchment to characterise the importance of short-term antecedent conditions to the response of the source waters

Table 1. Monthly rainfall characteristics recorded at the C2 weather station and ITE monthly rainfall collector during the study period.

Month	[1]mean rainfall (1980–1990)	[1]ITE gauge (mm)	AWS gauge (mm)	number of rain days (>0.18 mm)	[2]number of events
1991					
May		39.5	ns		
June		174	170	25	3
July		167	175	24	4
August		212	201	20	2
September		173	173	14	4
October		193	193	25	5
November		306	391	25	11
December		245	302	16	5
1992					
January	341	148	176	17	2
February	216	168	176	21	4
March	282	364	345	29	6
April	109	177	180	24	3
May	101	117	123	19	1
June	151	66	63	14	0
July	128	132	131	24	1
August	198	310	308	30	6
September	204	215	219	26	4
October	297	211	185	23	4
November	277	404	404	26	16
December	335	230	207	21	4

AWS = automatic weather station
ns = not sampled
[1] recorded by ITE monthly rainfall gauge situated just outside the C2 catchment
[2] rainfall which produced a runoff response in the stream of greater than 10 l s^{-1}

and hence stream flow in the catchment. Similar indices have been used elsewhere (Foster, 1979) to represent the diminishing impact over time of preceding rainfall events. The index takes the form;

$$ARI = \sum_{i=1}^{\infty} k^{i-1} R_{(t-i)}$$

where t is the day on which the event occurred, $R_{(t-i)}$ is the total runoff recorded on the day (t – i), and k is the coefficient between 0 and 1. Thus, the index is weighted towards the most recent conditions in the catchment; by using a value of k = 0.5, as here, runoff conditions over the preceding 7 days are represented.

The antecedent conditions, represented by the ARI, rainfall characteristics and the response of pipeflow, overland flow, throughflow and streamflow to rainfall for the seven storms sampled are presented in Table 2. The very low ARI for the event of 10 June 1991 was due to an unusually long period of dry weather preceding the event. In contrast, an event on the previous day resulted in larger ARIs for the events of 1 November 1991 and 11 March 1992. The short term antecedent conditions, rainfall intensity and duration of the storm all influence the response of the source waters and therefore streamflow. For example, on 10 June 1991, over 29 mm of rain fell, yet a peak discharge of only 3.2 l s^{-1} was observed. In contrast, on 3 July 1991, an intense shower of only 10.1 mm rain produced a similar streamflow response. Storms with very wet antecedent conditions were not intensively sampled as the ARI values for the sampled events are low compared to the ARI values of other events recorded during the study period as a whole; 23% of storms had an ARI of less than 10, 37% of storms had an ARI of between 10 and 20 and 40% of storms had an ARI of greater than 20.

The approximate contributions of pipe water from outlet PA and overland flow from the peat around the stream head to total and peak storm runoff from the catchment for each of the 7 events are given in Table 3. It is assumed that pipe water from the other pipe outlets in the catchment, overland flow from the steep side slopes around the stream and throughflow are the other major sources of runoff during storms. At peak streamflow, pipe water from outlet PA and overland flow from the stream head area contribute over 60% of storm runoff. Monitoring of the stream at two locations indicates that approximately 70% of all storm runoff reaches the stream above the upper weir, i.e. via the stream head area (Chapman, 1994). However, this is likely to be greater during summer events when the steep sideslopes adjacent to the stream channel are drier.

Stormflow Calcium and Magnesium Response

At low flows, stream water is derived mainly from drainage water which has had a long residence time within the catchment and thus contains high concentrations of base cations and bicarbonate released from weathering reactions (Reynolds *et al.*, 1986). Routine sampling of stream water from the catchment displays the frequently reported inverse relationship between stream discharge and concentrations of Ca and Mg (Reynolds *et al.*, 1983) attributed to stream water chemistry tending towards that of the storm source waters at high flow. However, during storms, both positive and negative relationships were observed between Ca and Mg concentrations and stream discharge (Fig. 2) and in some storms an initial increase in concentration was followed by dilution (Fig. 2). Therefore the response of Ca

Table 2. Hydrological data for the storms sampled.

	10.6.91	3.7.91	24.7.91	31.10.91	1.11.91	10.3.92	11.3.92
ARI	0.99	4.4	4.7	2.4	12.95	6.89	10.02
Total rainfall (mm)	29.2	10.1	30.2	27.0	23.0	17.8	27.4
Duration of storm (h)	18.5	2.05	8.45	11.25	3.05	9.15	8.0
Mean intensity of rainfall (mm/h)	1.58	4.90	3.45	2.40	7.55	1.95	3.42
Maximum 5 min rainfall (mm)	1.41	1.41	1.01	2.52	1.42	0.54	0.54
Maximum pipeflow (l s^{-1})	1.0	1.4	2.8	3.6	1.7	1.62	3.42
Time of peak pipeflow	04:50	08:00	14:00	13:45	12:15	11:30	16:45
Maximum overland flow (l s^{-1})	ns	ns	0.52	0.83	0.37	0.20	1.28
Time of peak overland flow	ns	ns	14:25	15:00	12:15	11:15	20:30
Maximum throughflow (l s^{-1})	ns	ns	0.25	0.21	0.21	0.13	0.26
Time of peak throughflow	ns	ns	14:15	15:00	12:15	11:30	20:30
Maximum streamflow (l s^{-1})	3.2	3.7	18.2	29.4	15.6	8.5	32.3
Time of peak streamflow	05:30	08:00	14:30	14:45	12:15	11:45	20:30
Total runoff (mm)	3.4	3.2	10.6	12.1	10.1	7.0	15.6

ARI = Antecedent runoff index
ns = not sampled

Table 3. The approximate contribution of overland flow, pipeflow from outlet PA and other waters to total storm runoff at the catchment outlet and (peak flow).

Storm	Overland flow	Pipe water from outlet PA	Other waters
10.6.91	ns	13% (33%)	ns
3.7.91	ns	10% (50%)	ns
24.7.91	41% (50%)	12% (16%)	53% (33%)
31.10.91	39% (50%)	11% (13%)	50% (37%)
1.11.91	40% (50%)	13% (13%)	47% (37%)
10.3.92	58% (50%)	25% (24%)	17% (25%)
11.3.92	47% (70%)	14% (14%)	39% (16%)

Other waters = pipe water from other outlets, throughflow and overland flow from other sources
ns = not sampled

and Mg cannot be represented by a simple relationship with stream discharge. This is confirmed by superimposition of stormflow Ca and Mg data on concentration versus stream discharge plots for monthly samples collected since 1980. These show that no discernible relationship exists between discharge and Ca or Mg concentrations (Fig. 3a and 3b).

As the predominant source of Ca and Mg is from mineral weathering, the concentration of these solutes in overland flow and pipeflow are lower than in throughflow and flush water, particularly for Ca. Concentrations of Ca and Mg in source waters varied little between events, except for the event of 10 June 1991 when concentrations were considerably higher in overland flow (Table 4). This may be attributed to the combined effects of dry deposition on the vegetation and the evapotranspiration of wet deposition producing an accumulation of salts on the surfaces of vegetation and soil during the preceding dry weeks. The response of Ca and Mg to storm events will depend partly on the chemical composition of the contributing waters from different sources. In all the storms, the major sources of runoff had considerably lower concentrations of Ca and to a lesser extent Mg than those observed in the pre-event stream water (baseflow) (Table 4). However, only in the storms of March 1992 did stream water Ca and Mg concentrations decline significantly through the events (Fig. 2e). In addition, the range of Ca and Mg values observed at the catchment outlet does not lie within the boundary defined by the chemical composition of pipe water, overland flow and pre-event stream water (baseflow) for individual events (Fig. 4). Therefore the response of stream water Ca and Mg during events cannot be explained by the simple mixing of storm runoff waters with pre-event stream water.

Table 4. Mean (and range) of Ca and Mg concentrations (mg l^{-1}) in catchment waters during the sampled events.

Storm	n	Pipeflow	n	Overland flow	n	Through flow	n	Flush water	Baseflow	Stream water
Calcium										
10.6.91	3	0.29 (0.28–0.30)	2	0.68 (0.66–0.70)		ns	4	1.38 (1.34–1.40)	ns	(1.30–1.80)
3.7.91	3	0.21 (0.20–0.22)	2	0.25 (0.22–0.28)		ns	2	0.77 (0.76–0.78)	1.02	(1.02–1.32)
24.7.91	7	0.15 (0.12–0.20)	5	0.22 (0.14–0.40)	5	0.55 (0.48–0.62)	3	0.74 (0.66–0.78)	1.02	(0.98–1.14)
31.10.91 & 1.11.91	9	0.35 (0.32–0.38)	3	0.39 (0.36–0.44)	9	0.62 (0.54–0.68)	2	0.74 (0.60–0.88)	1.17	(1.02–1.32)
10.3.92 & 11.3.92	7	0.21 (0.18–0.24)	3	0.23 (0.22–0.24)	6	0.66 (0.54–0.74)		ns	0.96	(0.74–1.14)
Magnesium										
10.6.91	3	0.83 (0.80–0.86)	2	1.30 (1.26–1.34)		ns	4	1.33 (1.30–1.63)	ns	(1.02–1.20)
3.7.91	3	0.43 (0.40–0.46)	2	0.47 (0.44–0.50)		ns	2	0.71 (0.70–0.72)	0.74	(0.72–0.89)
24.7.91	7	0.39 (0.36–0.42)	5	0.43 (0.39–0.50)	5	0.57 (0.52–0.60)	3	0.63 (0.58–0.66)	0.70	(0.66–0.78)
31.10.91 & 1.11.91	9	0.53 (0.50–0.56)	3	0.49 (0.44–0.56)	9	0.64 (0.60–0.66)	2	0.62 (0.56–0.68)	0.69	(0.69–0.90)
10.3.92 & 11.3.92	7	0.42 (0.38–0.46)	3	0.47 (0.34–0.72)	6	0.64 (0.53–0.74)		ns	0.72	(0.60–0.76)

n = number of samples
ns = not sampled

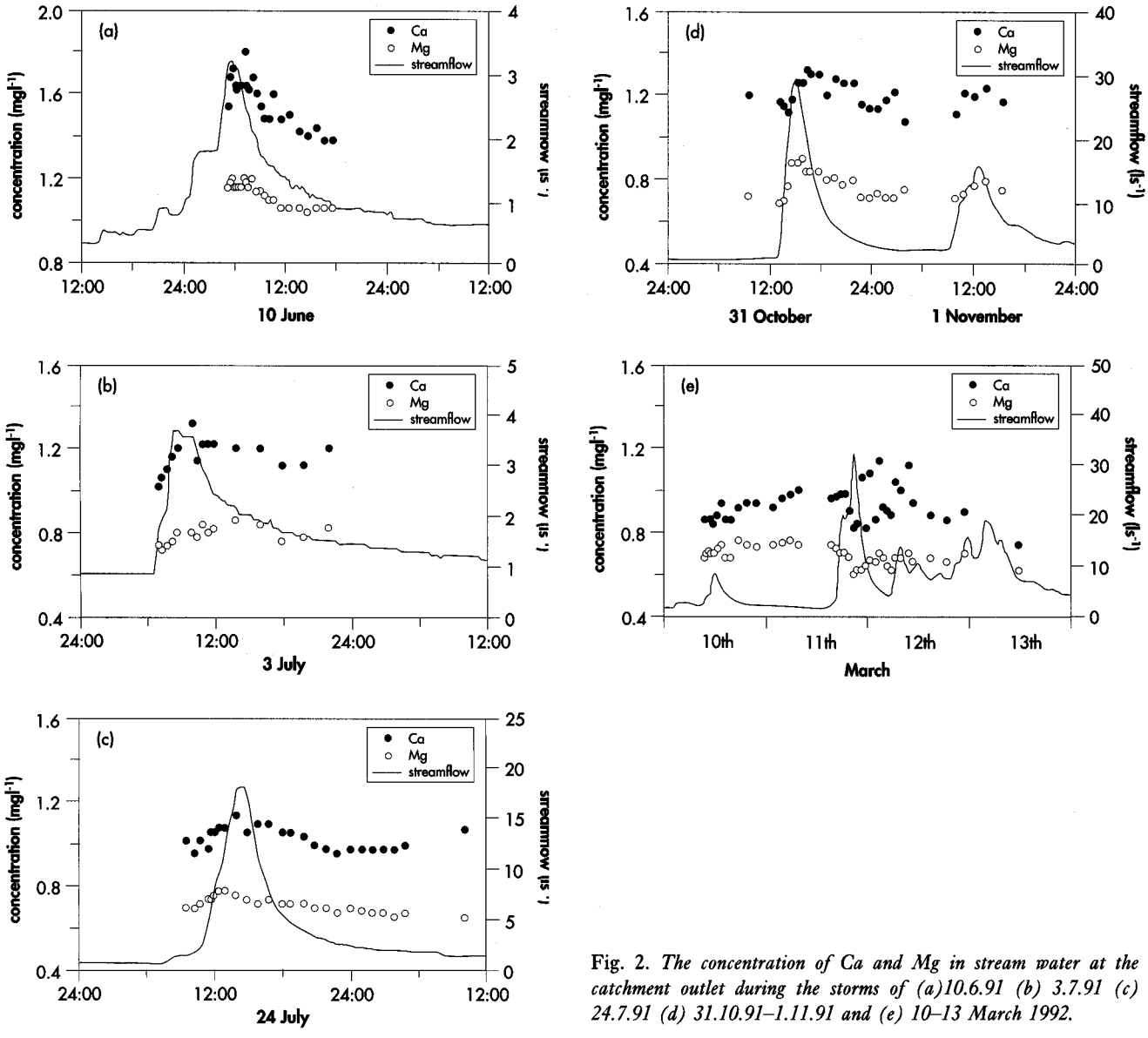

Fig. 2. *The concentration of Ca and Mg in stream water at the catchment outlet during the storms of (a)10.6.91 (b) 3.7.91 (c) 24.7.91 (d) 31.10.91–1.11.91 and (e) 10–13 March 1992.*

Hornung *et al.* (1986a) and Muscutt *et al.* (1990) also observed high concentrations of Ca in the C2 stream during both low and high flows but were unable to identify the source, other than calcite veins, which are known to occur in the area. Muscutt *et al.* (1990) observed a mean Ca concentration of 1.7 mg l^{-1} in flush water following a dry period in July 1988, and proposed that the flush may be a zone of active weathering and flow along a calcite vein. Although similar Ca concentrations were observed for flush water in the small event of 10 June 1991 (Table 4), which also followed a dry period, intensive sampling of the flush water during the other events in this study showed that although flush water contained higher concentrations of Ca and Mg than pipe water and overland flow (Table 4), it was not high enough to account for the observed stream responses of Ca during storms.

The exact source of the water feeding the stream at baseflow is unknown, but its chemical composition has been inferred from stream water samples taken during dry weather baseflow in June 1992, when concentrations of Ca and Mg were 1.62 and 0.96 mg l^{-1}, respectively. These values are slightly lower than the highest concentrations of Ca (1.8 mg l^{-1}) and Mg (1.2 mg l^{-1}) observed during the event of 10 June 1991. Muscutt *et al.* (1990) also observed an increase in Ca and Mg in stream water to a maximum of 2.2 and 1.1 mg l^{-1} respectively, during a storm in June 1989. Assuming dry weather baseflow is representative of water with a long residence time within the catchment (which will be referred to as groundwater), even a large contribution from this source cannot account for the observed response. Furthermore, this mechanism would not accord with the hydrological monitoring which indi-

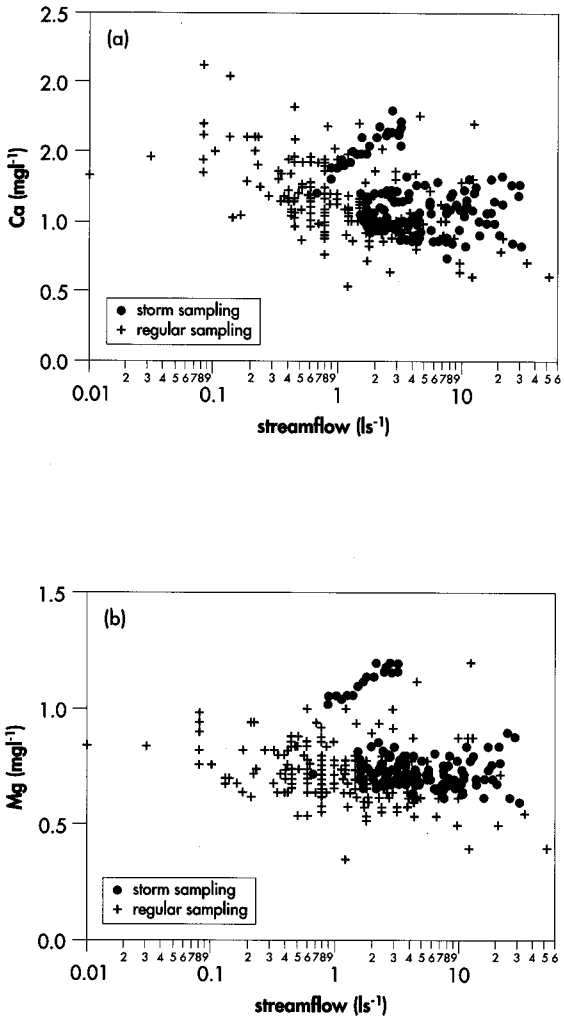

Fig. 3. *The relationship between streamflow and (a) Ca and (b) Mg concentrations at the catchment outlet.*

cates that overland flow and pipeflow, together with throughflow, are the major sources of storm runoff in the catchment. Although much dry and occult deposition will probably have accumulated on the vegetation prior to the events of June 1991 and June 1989, Ca and Mg concentrations in overland flow were considerably lower than those observed in stream water (Table 4; Muscutt *et al.*, 1990)

Processes Controlling Ca and Mg in Pipe Water along its Stormflow Pathway

CHEMICAL CHANGES ALONG THE STORMFLOW PATHWAY

During all events, a large increase in the concentrations of Ca and Mg in pipe water was observed along the pathway between outlet PA and the stream channel, a distance of 55 m; Ca increased by between 68% and 90%, while Mg increased by up to 57%. A corresponding decrease in H^+ concentration (Fig. 5a) was observed with most of the change in concentration of these solutes focused over a distance of only 10 m.

The largest changes in Ca, Mg and H^+ concentrations were observed during the small event of 10 June 1991, which was preceded by a period of six weeks without pipeflow (Table 5). In contrast, the event of 11 March 1992, which followed an event on the previous day, displayed the smallest changes in concentrations. This suggests that the dryness of the period between events affects the changes in Ca and Mg concentrations along the pathway directly. The general inverse relationship between the ARI and the magnitude of change in concentration of these solutes between sampling location PA3 and the stream head (Fig. 6) confirms this observation. The scatter in the relationship with ARI reflects the influence of factors such as rainfall intensity which will determine the velocity of pipe water flowing along the pathway and hence the contact time with the soil surface.

The changes in Ca and Mg concentration of pipe water occur rapidly over a short distance and could be explained by the mixing of pipe water with a significant quantity of unidentified storm runoff which is low in acidity and enriched in base cations. However, visual inspection of the stream head area suggests that the majority of the water reaching the stream via this pathway originates from pipe outlet PA. Furthermore, the relationship between antecedent conditions and the magnitude of change in Ca, Mg and H^+ concentrations suggests that Ca and Mg accumulate along the pathway between events. The reduction in the magnitude of change in acidity and the concentrations of Ca, Mg as events progress (Chapman *et al.*, 1993), and in successive events, suggests that the store of Ca and Mg becomes depleted as events progress and during periods of sustained high flow. This response suggests strongly that the changes in Ca and Mg concentrations along the pathway are controlled either by rapid dissolution or cation exchange reactions within the soil.

CHEMICAL CHARACTERISTICS OF SOIL ALONG THE STORMFLOW PATHWAY

Exchangeable Ca and Mg concentrations varied considerably between locations along the pathway (Fig. 7). At some sites, concentrations decreased down the profile whilst at others, little variation with depth was observed. The largest concentrations were measured in soil samples from all depths at location 2 and in the top 10 cm at location 3 where exchangeable Ca ranged between 6.3 and 7.3 cmol kg^{-1} dry soil and exceeded the amount of exchangeable Al. In contrast, at the other locations exchangeable Al ranged between 5.9 and 10.3 cmol kg^{-1} and exceeded the total amount of exchangeable base cations in the soil at 0–10 cm depth. The pH of the 0–10 cm soil layer reflected the base

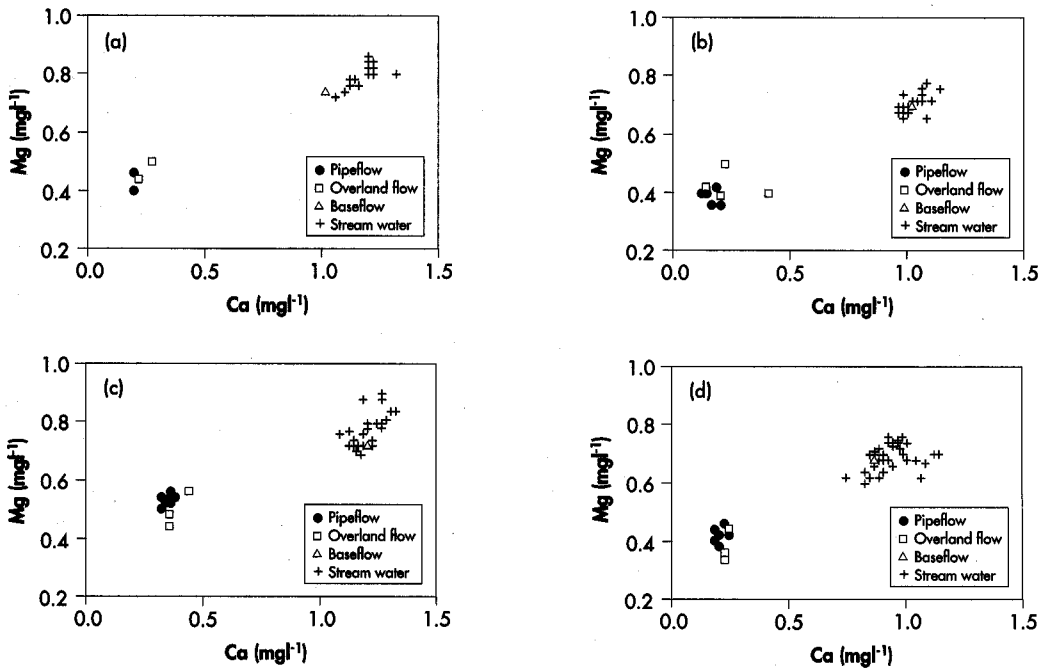

Fig. 4. *Mixing diagrams for Ca versus Mg for the C2 catchment for the storms of (a) 3.7.91 (b) 24.7.91 (c) 31.10.91–1.11.91 and (d) 10–13 March 1992.*

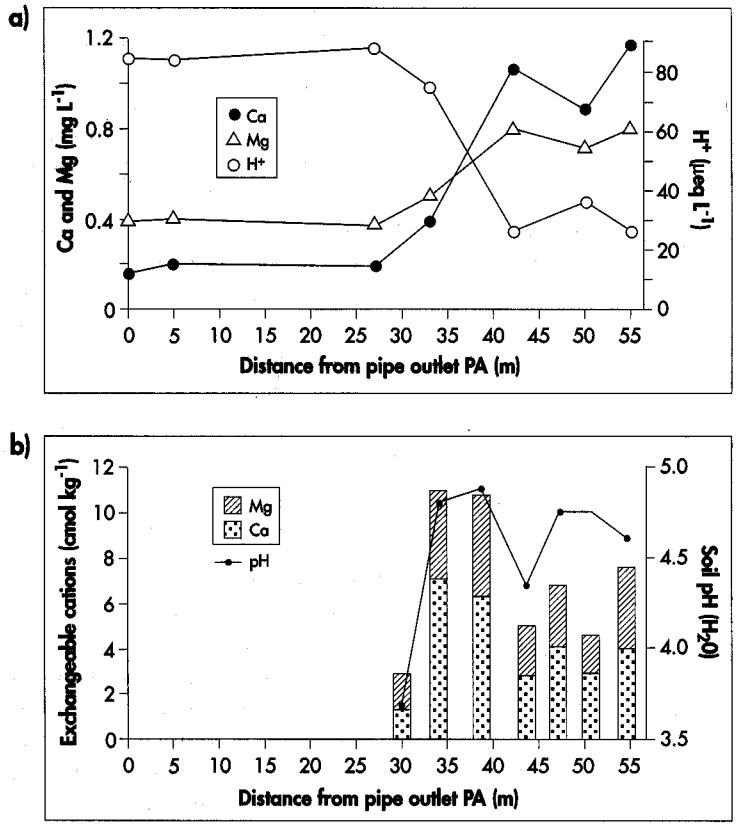

Fig. 5. *(a) Mean concentrations of Ca, Mg and H^+ in storm runoff between the pipe outlet PA and the stream channel during the event of 24 July 1991. (b) Soil pH and mean exchangeable Ca and Mg in soil from the 0–10 cm depth between the pipe outlet PA and the stream channel.*

Table 5. Mean change in concentrations (μeq l^{-1}) of Ca, Mg and H^+ between pipe outlet PA and the head of the stream.

Storm	Ca	Mg	H^+
10.6.91	78.8	46.9	−129.6
3.7.91	57.9	37.0	−78.0
24.7.91	49.4	28.8	−57.4
31.10.91	45.9	25.5	−75.0
1.11.91	39.9	24.7	−69.5
10.3.92	33.4	26.3	−73.2
11.3.92	28.9	16.4	−77.0

saturation of the soil, with the lowest soil pH of 3.68 coinciding with the lowest exchangeable divalent cations at location 1 and the highest soil pH coinciding with highest exchangeable divalent cations at locations 2 and 3 (Fig. 5b).

The amounts of exchangeable cations in the soil profile at location 1 were very similar to those found in stagnopodzol soils under grassland elsewhere at Plynlimon (Reynolds *et al.* 1988). In contrast, the other soils sampled along the stormflow pathway had much higher concentrations of exchangeable Ca and Mg than generally encountered in acid upland soils (Hornung *et al.*, 1986b). At locations 2 and 3, amounts of exchangeable divalent base cations were relatively enriched compared to the other sites along the transect and even exceeded concentrations observed in several agriculturally improved soils at Plynlimon; only in the O horizon of a recently ploughed and limed soil were concentrations greater (Hornung *et al.* 1986b). Moreover, the largest decreases in pipe water acidity and increases in Ca and Mg concentrations during storm events were observed at these enriched locations (Fig. 5a&b).

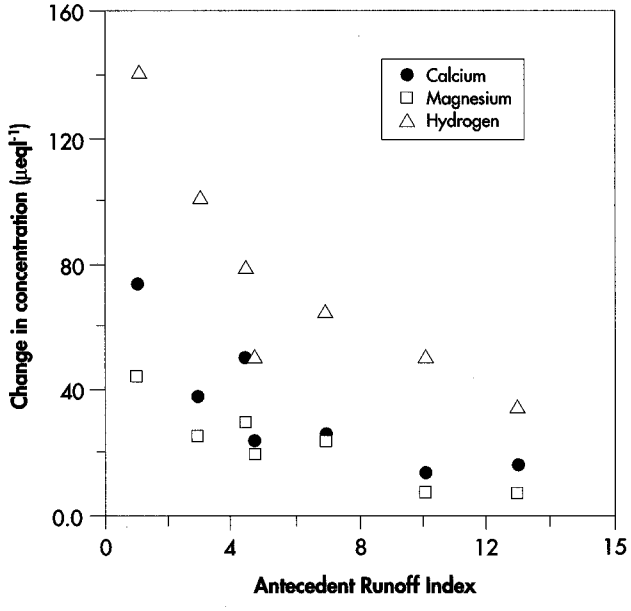

Fig. 6. *The relationship between the antecedent runoff index (ARI) and the mean change in Ca, Mg and H^+ concentrations between sampling point PA3 and the stream channel during the seven events sampled.*

LABORATORY INVESTIGATION OF ION EXCHANGE REACTIONS

The laboratory investigation successfully simulated the changes in pipe water chemistry observed during storms in the field (Table 6). Following passage over the soil, samples of pipe water became less acidic and were enriched by a roughly equivalent amount of Ca and Mg (Table 6; Fig. 8). In general, the magnitude of change in concentrations of H^+, Ca and Mg decreased as each subsequent sample of pipe water passed over the soil (Fig. 8) showing that the store of base cations was progressively depleted. This result is consistent with the decrease in magnitude of chemical change observed in successive sets of pipe water samples taken along the pathway during storms (Chapman *et al.*, 1993).

CONTROLS OF CHEMICAL CHANGES ALONG THE STORMFLOW PATHWAY

The field and laboratory results are consistent with the hypothesis that pipeflow acidity and concentrations of Ca and Mg along the storm flow pathway are controlled by ion exchange reactions in an area of soil locally enriched with exchangeable Ca and Mg. However, to support this hypothesis, there must be a source of Ca and Mg in the region to replenish the soil exchange complex. The C2 catchment is underlain by colluvium derived from Frongoch mudstones containing very low concentrations of Ca (CaO=0.04% w/w), which is reflected in the low Ca status of stagnopodzol soils and soil solutions in the catchment (Hornung *et al.*, 1986a). Consequently, the large concentrations of Ca observed in streams draining some catchments at Plynlimon have been attributed to the weathering of localized veins of calcite which are known to occur within the area (Reynolds *et al.*, 1986). Such veins may be present within the C2 catchment and the stream head area may also contain calcite-bearing drift material. Weathering of either of these would produce readily soluble Ca, and to a lesser extent Mg, which could accumulate on soil ion exchange sites. However, analysis for 'free lime' indicated that no free $CaCO_3$ or $MgCO_3$ was present in the soils sampled along the stormflow pathway. Thus, weathering reactions cannot provide an immediate and proximal source of Ca or Mg implying that an external source and transport mechanism must be invoked.

The stream head area is saturated for most of the year, as indicated by the abundance of *Juncus* and *Sphagnum* vegetation, as a slow seepage of water emerges at the surface. This seepage water was sampled and found to

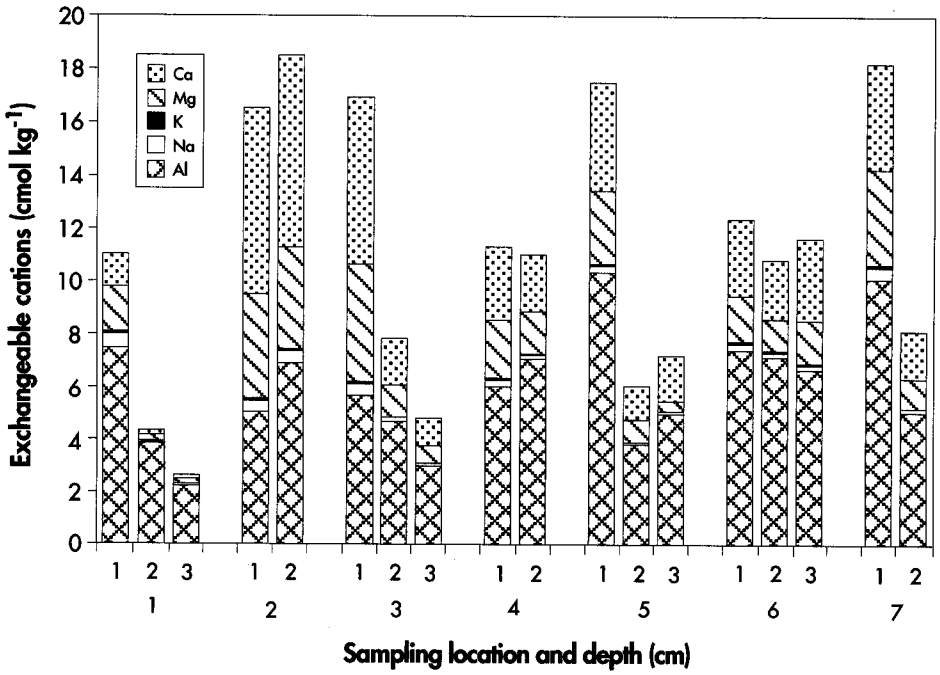

Fig.7. *Exchangeable Al, Na, K, Mg and Ca at 7 locations along the stormflow pathway at (1) 0–10 cm, (2) 10–30 cm and (3) >30 cm depth.*

contain relatively large amounts of Ca (1.12 mg l^{-1}) and Mg (0.79 mg l^{-1}) compared to other source waters in the catchment (Chapman, 1994). More recently, ten bore holes have been drilled in the neighbouring Hafren and Hore catchments revealing the presence of very base-rich water at varying depths beneath the surface (Neal *et al.*, 1997a). The mean Ca concentration of water samples from nine of the bore holes range between 0.89 and 3.67 mg l^{-1}, while one bore hole has a mean Ca concentration of 16.08 mg l^{-1} (Neal *et al.*, 1997a.). The dynamics of the groundwater response to rainfall is currently under investigation, but preliminary results indicate that the groundwater supply is large and geographically extensive.

Table 6. Concentration (μeq l^{-1}) of H^+, Ca and Mg in pipe water before and after passing over soil from the 0–10 cm depth at sampling location 2.

Sample	H^+	Ca	Mg
Pipe water	70.8	13.0	27.1
After passing over soil			
1	17.8	39.9	41.1
2	21.4	43.9	44.4
3	21.4	43.9	44.4
4	36.3	30.9	39.5
5	33.1	35.9	39.5
6	32.4	33.9	41.1
7	31.6	34.9	41.1
8	34.7	34.9	42.8
9	47.9	29.9	37.8
10	50.1	25.9	39.5

From the data presented in this study, the following mechanism is proposed to account for the observed changes in the chemical composition of pipe water emitted at outlet PA along its flow pathway to the stream. Groundwater enriched in Ca and Mg, similar to that observed in the neighbouring Hore and Hafren catchments, seeps slowly to the surface between soil sampling locations 2 and 3 which coincide with changes in slope, soil type and vegetation. This water may be flowing along a geological faultline which runs along the north-western boundary of the catchment. These fault zones are common at Plynlimon (Chapman, 1986) and frequently contain calcite mineralisation (Hornung *et al.*, 1986a). As groundwater passes either laterally or upwards through the shallow, organic rich soil, Ca and Mg are adsorbed onto the soil exchange sites. Upward water movement would account for the large exchangeable Ca and Mg concentrations throughout the soil profile at location 2 compared to soils at the other locations along the flow pathway and is consistent with the artesian groundwater flow observed elsewhere at Plynlimon (Neal *et al.*, 1997a). During storms, acidic, base cation depleted pipe water passes over this area *en route* to the stream and H^+ ions in solution are exchanged for Ca and Mg held on the soil exchange sites. Antecedent conditions have a direct effect on the magnitude of chemical change in the pipe water as the size of the

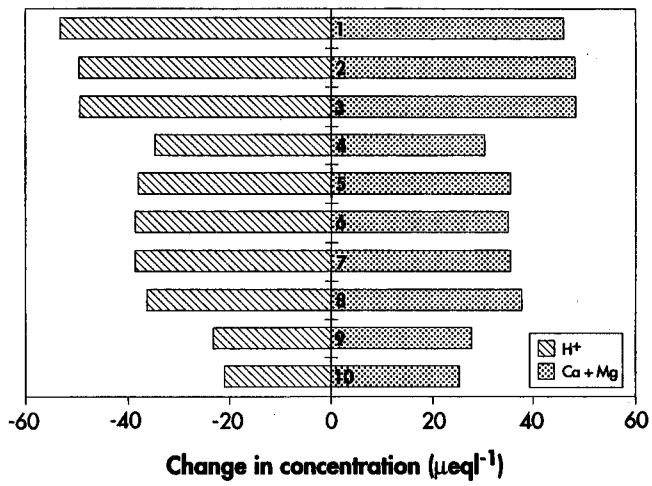

Fig.8. *The decrease in H^+ concentration relative to the increase in Ca and Mg concentration in all samples of pipe water passed over soil from the 0–10 cm depth at location 2.*

exchangeable Ca and Mg pool is determined by the frequency and duration of storm events. A long elapsed time between events allows for greater accumulation of Ca and Mg on the exchange sites resulting in a large change in pipe water chemistry during the ensuing storm event. As events progress, the divalent base cation stores become depleted. Therefore, antecedent flow conditions and the magnitude of the event control the degree to which the stream is buffered against inputs of acidic pipe water and hence the acidity and Ca and Mg content of stream water.

Implications

The Plynlimon catchments are located in an area of ancient base-poor bedrock overlain by acid, base-depleted soils. Given this background, numerous studies have struggled to explain some of the base-rich chemical characteristics of stream water chemistry observed within the catchments (e.g. Hornung *et al.*, 1985; Reynolds *et al.*, 1986; Neal *et al.*, 1992). Applications of EMMA at Plynlimon have also failed to explain stream water chemistry satisfactorily as a mixture of the observed (sampled) source waters, i.e. acid soil waters and alkaline baseflow (Christophersen *et al.*, 1990; Neal *et al.*, 1990). These results have been attributed to the use of incorrect end-members or the presence of additional, unobserved end-members comprising soil water with a high Ca content or groundwater enriched in base cations, which become a major source to streams during events (Neal *et al.*, 1990).

The results from this study suggest that groundwater can influence storm runoff chemistry directly through the modification of pipe water along a hydrological pathway. The proposed mechanism is indirect, via the local enrichment of soil exchangeable Ca and Mg at the point where groundwater emerges at the surface and, as has been clearly demonstrated, the effects on storm water chemistry at the scale of the C2 catchment are highly significant. Groundwater may affect storm runoff more widely along other stormflow pathways in the C2 catchment. For example, water sampled from the flush during storms was less acidic and contained higher concentrations of Ca and Mg than overland flow sampled at the head of the flush, suggesting that groundwater may also seep to the surface beneath the flush and similar ion exchange reactions occur here as observed along the pipe water pathway during storms. This, therefore, has important consequences for the degree to which the stream is buffered against inputs of acidic storm runoff and implications for modelling stormflow response. Conventional EMMA is unable to represent such modification to end-member chemistries along flowpaths.

Direct neutralisation of pipeflow acidity through mixing with groundwater along the stromflow pathway is probably a minor process at this site as groundwater flow rates are insufficient and the field hydrological and chemical monitoring, plus laboratory data, support the proposed ion exchange hypothesis. However, recent installation of boreholes in the headwaters of the Severn at Plynlimon has shown that an extensive, shallow groundwater fracture flow system exists (Neal *et al.*, 1997a). The groundwater is alkaline and is both geographically extensive within the catchments and capable of producing quite large flow rates with some boreholes becoming artesian under wet, winter conditions (Neal *et al.*, 1997a). Clearly groundwater influences the chemical composition of base flow directly and provides an explanation for the field observations at Plynlimon (e.g. Reynolds *et al.*, 1986).

The extent to which groundwater participates in the chemical modification of storm runoff elsewhere at Plynlimon is presently unknown. Other surface expressions of groundwater have been observed in the field both by the authors and Neal *et al.*, (1997a; 1997b) whilst further stream inputs have been identified or inferred geochemically. For example, a recent low-flow spatial hydrochemical survey identified a very localised input of alkaline water to the Hore catchment (Locks 1996). In this case, stream alkalinity increased from −7 to +162 μeq l^{-1} and Ca from 0.6 to 3.4 mg l^{-1} in a distance of 250 m. A similar 'alkaline anomaly' was identified in a summer baseflow survey of the acidic Cwm catchment at Llanbrynmair approximately 10 km north of Plynlimon (Hudson *et al.*, 1996). Amongst the chemically distinctive group of 3 small tributaries at the centre of the catchment, Ca concentrations as high as 8 mg l^{-1} were observed with pH values in excess of 7. These waters were also the coldest sampled in the catchment, giving further evidence of a groundwater origin. Peat soils sampled near the tributaries had anomalously large exchangeable divalent base cation concentrations, reaching a maximum of 26 cmol kg^{-1} dry soil of Ca and 10 cmol kg^{-1} dry soil of Mg, which are between 10 and 50 times greater than observed elsewhere in the catchment, suggesting that these peats have been flushed by alkaline groundwater (ITE unpublished data). Thus, while the importance of localised groundwater

inputs for baseflow chemistry is clear, further work is required to determine whether these and other surface expressions of groundwater identified at low flows play a significant role in modifying the chemistry of acidic soil runoff water during storms, either by direct contribution to streamflow, or through the ion exchange processes identified within the C2 catchment.

The role of groundwater in influencing stream water chemistry at both low and high flows is not unique to the Plynlimon catchments. Hydrological and chemical observations from the Allt a'Mharcaidh catchment in NE Scotland suggest that base-rich water at a depth of 2–3 m in the riparian zone influences the chemistry of baseflow, maintaining high alkalinity, pH and base cations (Jenkins *et al.*, 1990). Hydrological modelling using EMMA suggests that this 'groundwater' is the dominant contributor to runoff (>50%) (Ogunkoya and Jenkins, 1991). However, the Ca content of this groundwater is not of sufficiently high concentration to account for the observed rise in stream water Ca concentrations during a storm in June 1989 if mixing with only soil and rain water is assumed (Jenkins *et al.*, 1994). Therefore, Jenkins *et al.*, (1994) proposed that Ca is mobilized from soil exchange sites by rain and soil water which are transmitted rapidly along preferential pathways. Thus, as observed in the C2 catchment at Plynlimon, the influence of groundwater on stream water chemistry during storms appears to be indirect at the Allt a'Mharcaidh.

The results from this study and others, which draw attention to the influence of base-rich groundwater on stream water chemistry, also have major implications for the validity of current estimates for freshwater critical loads. At present, the calculation for freshwater critical loads, which was proposed by Henriksen (1984), assumes that the major sources of base cations in stream water are from non-marine derived atmospheric inputs and the weathering of parent material. Inputs of base cations from groundwater sources are not taken into account; this may be a major oversight in determining the critical load for freshwaters in many upland catchments.

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